



Consumer and
Corporate Affairs Canada

Consommation
et Corporations Canada

(11) (A) No. **1 162 054**
(45) ISSUED 840214

(52) CLASS 53-168

(51) INT. CL. ³ C22B 11/00

(19) (CA) CANADIAN PATENT (12)

(54) PROCESS FOR THE RECOVERY OF PLATINUM GROUP METALS
FROM REFRACTORY CERAMIC SUBSTRATES

(72) Day, Joseph G.,
U.K.

(73) Granted to Johnson, Matthey & Co., Limited
U.K.

(21) APPLICATION No. 366,950
(22) FILED 801217
(30) PRIORITY DATE U.K. (7944656) 791231

NO. OF CLAIMS 24 - NO DRAWING

Canada

DISTRIBUTED BY THE PATENT OFFICE, OTTAWA.
CCA-274 (11-82)

ABSTRACT

A process for recovery of platinum group metals (PGMs) from refractory ceramic substrates containing an aluminium silicate and/or alumina, for example, wash-coated auto emission control catalysts and Pt reforming catalysts. A charge, in divided form, containing the substrate, one or fluxes and a collector is heated in a high heat intensity furnace, to a temperature of at least 1420°C to produce a molten metallic phase including a substantial proportion of the said metals and a molten slag phase. These are then separated and the platinum group metals subsequently extracted from the metallic phase. By choice of suitable fluxes, at least some alumina can be converted to an aluminium silicate which becomes molten at the operating temperature. Further, the ability to use high temperature fluxes avoids the need for an excessive slag which is normally required to dissolve the high alumina content of such catalysts and which normally gives rise to unacceptable losses of the metals to be recovered when applying conventional pyrometallurgical techniques.

A PROCESS FOR THE RECOVERY OF PLATINUM GROUP METALS FROM REFRACTORY CERAMIC SUBSTRATES

This invention relates to the recovery of platinum group metals which may be present in artefacts made from refractory materials, that is to say, to the secondary refining of such metals as opposed to primary refining - from the ore.

The high melting point of refractory based substrates which contains platinum group metals (PGM), in particular alumina substrates, presents a severe slag problem when attempts are made using conventional pyrometallurgical processes.

10 Blast and reverberating furnaces normally operate at temperatures in the range 1250 - 1350°C which is considerably below the melting point of alumina. At these temperatures, therefore, it is necessary to include in the charge, slags such as Wollastonite or Olivine in order to dissolve the alumina but only 15% alumina can be dissolved without detriment to the melting point and viscosity. Many refractory ceramic substrates, however, have an alumina content much higher than 15%. Automobile emission control catalysts with aluminium-silicate (e.g. cordierite and mullite) substrates contain 35% alumina and up to 46% when wash coated. To apply conventional pyrometallurgical process to such catalysts 20 therefore necessitates the use of sufficient flux to maintain an upper limit of 15% Al_2O_3 but this is economically non-viable, not least because the loss of PGM in the increased quantities of slag is unacceptable.

What we now propose, in accordance with the present invention, is a process for the recovery of platinum group metals deposited on or contained in a refractory ceramic substrate containing an aluminium silicate and/or alumina, comprising preparing, in divided



form, a charge containing the refractory substrate bearing the said metals, one or more fluxes, and a collector material or collector material precursor, for the metal or metals to be recovered, heating the charge to a temperature of at least 1420°C to produce a molten metallic phase containing a substantial proportion of the said metal or metals, and a molten slag phase containing flux, ceramic residues and the remainder of the said metals, separating the two phases, and separating the platinum group metals from the metallic phase.

10 The flux or fluxes are preferably selected from the groups consisting of CaO, CaF₂, BaO, Fe₂O₃, MgO, SiO₂ and TiO₂.

By heating a charge containing cordierite to at least 1420° (i.e. above the melting point of the cordierite), the amount of slag needed to dissolve the alumina can be reduced. In the case of substrates having an alumina wash coat or which consists of alumina, (e.g. a Pt reforming catalyst) at least some of the alumina, which is a precursor for aluminium-silicate, can be converted to an aluminium-silicate and so can become molten at the operating temperature, by adding to the charge, a SiO₂ and/or a MgO, flux. With an alumina substrate acceptable recovery is possible without the addition of SiO₂ and/or MgO, but only by including in the charge a flux content approximately equal in weight, to the alumina content.

If the substrate contains another aluminium silicate it may be necessary to operate at a higher temperature. Examples of other aluminium silicates are mullite, sillimanite, petalite, spodumine and andalusite.

30 In addition, however, the use of operating temperatures higher than heretofore applied in secondary refining, enables the use of the high temperature fluxes specified whereby the alumina present, even where the substrate is wash coated, can be dissolved without excessive

quantities of flux.

The melting point of aluminium-silicates such as mullite (aluminium-silicate) or cordierite (magnesium-aluminium silicate) is in the region of 1420°C but with the addition of an alumina wash-coat the melting point of the substrate is increased to about 1650°C. In order to produce a fluid slag with a low viscosity and hence optimise recovery, the operating temperature needs to be about 100°C above the melting point of the substrate and we, therefore, prefer operating temperatures in the range 1500-1750°C. Such temperatures can be achieved using high heat intensity furnaces, for example, submerged electric arc furnaces and plasma-arc furnaces, which latter furnaces are known for primary refining but not for secondary refining.

Because submerged electric arc furnaces produce undesirable agitation of the charge, plasma arc furnaces are to be preferred and we have tested a variety of different types inter alia furnaces incorporating expanded plasma systems, furnaces having a static gun, extended arc furnaces including a transferred plasma arc furnace. Only furnaces adapted for batch operation have been tried but a continuous operation furnace with provision for continuous removal of the slag and/or metallic phases could be used. The process of this invention is operable with all types of high heat intensity furnaces tested though with varying degrees of success. It is considered, however, that the differences in recovery obtained were related primarily to the charge formulation and only to a limited extend upon the type of furnace used.

Suitable gases for the plasma are argon, helium, or nitrogen and we have found that it is even possible under some circumstances to use air, which is considerably cheaper than the alternatives. With air, however, there is a tendency to oxidise iron with attendant loss of iron into the slag.

The divided charge is fed gradually into the furnace through the plasma arc and, in batch processes, it is desirable to continue the discharge of the plasma arc for a minimum holding period after passing the entire charge therethrough, the minimum holding period preferably being from 5 to 30 mins.

Automobile emission control catalysts may be in one of two basic forms namely a monolithic structure or in pelletized form. The charge is prepared by mixing in suitable proportions the catalyst material reduced to a finely divided form by crushing or otherwise 10 or, depending upon the pellet size, in the form of pellets, with the flux or fluxes and collector material or materials. If desired a monolith catalyst or large pellets may be reduced by (e.g.) crushing and mixed with the selected flux(es) and collector material(s), the mixture then being compacted to produce pellets. A binder material preferably in an amount of 2% by wt of the mixture, can be used to ensure adequate green strength.

The grain size of the charge is selected inter alia to ensure intimate contact between the catalyst material, the fluxes and the collector and to avoid undue losses by entrainment in the gas flow 20 through the plasma furnace.

It is preferred to reduce the catalyst to the range minus 10-minus 200 mesh but in trials we have conducted, the best results have been obtained at minus 8 mesh (2.8 mm).

Satisfactory results have, however, been obtained using raw autocat pellets measuring 3 mm x 6 mm and pellets compacted from a finely divided mixture of the refractory substrate, flux and collector, having a diameter of $\frac{3}{8}$ ".

As for the collector material, this is preferably present 30 in an amount of 2-10% by weight (of the refractory material) and in the preferred embodiment, iron is used either in the form of iron powder or filings or cast iron shavings. Alternatively, the

iron can be produced in situ by the addition of an oxide of iron, such as hematite and a reducing agent such as carbon, to the charge. Other collector materials may be used, e.g. copper, nickel, cobalt, lead, aluminium or mixtures thereof.

The choice of flux or fluxes, which may be present in an amount of up to 100% by weight (of the refractory material content), depends to a large extent upon the particular refractory material from which the PGM's are to be recovered. As stated above MgO and/or SiO₂ are useful to convert alumina to aluminium silicate (e.g. cordierite). We have found that CaO is particularly efficient in producing good recovery and is a preferred component of the flux. Another preferred flux component is CaF₂ which has a high solubility in the refractory oxide, alumina.

The operating temperature of the plasma should be kept to the minimum consistent with the production of a low viscosity slag and satisfactory recovery of platinum group metal. Both Fe₂O₃ and CaO are beneficial in lowering the melting point and viscosity of the slag.

Separation of the slag and metallic phases, and separation of the platinum group metals from the metallic phase, after cooling thereof, may be effected by any suitable method known to those skilled in the art.

EXAMPLES 1 TO 10

Preparation of Charge

Automobile emission control catalysts hereinafter referred to as "autocat" consisting of Pt, Rh, and NiO deposited upon an Al₂O₃ washcoated cordierite ceramic refractory were jaw crushed to minus 8 mesh (2.8 mm). An analysis of the "as received material and the crushed catalyst" showed very good agreement, which suggests that any fines that were lost during the crushing operation did not contain a significantly higher proportion of platinum group metals.

Samples of the crushed catalyst from three of the trials were analysed, the results were as follows:

	<u>% by weight</u>		
	Pt	Rh	Ni
Trial 6	0.21	0.026	0.67
Trial 9	0.21	0.025	0.55
Trial 10	0.19	0.023	0.58

10 The relevant fluxes were added as powders from standard laboratory reagents, the lime was added as $\text{Ca}(\text{OH})_2$. The iron collector was added as iron sponge or as gray cast iron shavings with a particle size similar to the crushed catalyst. The whole charge was handmixed and fed into a hopper.

Plasma

Because of the small scale of the operation a static plasma arc furnace was used and melting was carried out either in salamander, suprex or graphite crucibles.

20 In the initial trial the charge from the hopper was screw fed into the crucible via three plastic tubes. The tubes were kept cool by the passage of argon. In order to maintain the plasma a flow of argon is passed through the water cooled plasma gun. With this relatively high gas velocity, it is possible that any fines in the charge might be blown through the system. In order to minimise such losses all subsequent trials used a single feed tube, thus reducing the argon throughput.

30 A known weight of charge was put into the hopper for each trial. A total of ten trials detailed in the following examples were carried out nine with a nominal charge of 5 kg catalyst with the last trial at the 10 kg scale. The feed rate to the plasma was 0.5 kg min^{-1} in all the trials. When all the charge had melted, a fluid melt was maintained for a minimum holding time. After the requisite holding period the power was switched off, the

refractory insulating box removed and the crucible and contents withdrawn. The products were physically removed from the crucible in each trial. The slag was broken into pieces with a hammer and any visible metal prills removed. The balance of the slag was crushed and split riffled to give an assay sample. The brittle metallic collector button was broken and TEMA* milled to produce a representative sample for assay. The platinum group metal recoveries were calculated on the weights and assays of the melted products.

10 No attempts were made to collect the fume from the trials, and the exit gases were allowed to burn and escape to the atmosphere. The exact loss due to fume was not established; however, a sample of the fume that had condensed in the exhaust tube over several runs and could not, therefore, be associated with any particular trial was analysed. The results showed that it contained 0.05% Pt and 0.008% Rh.

20 The results achieved in the Examples 1 to 10 are set out in Table 1. It will be seen that direct melting of the autocat at 1700°C with 5% Fe gave poor coalescence of the collector and resulted in numerous prills in the slag. The addition of 30% $MgO+SiO_2$ to convert the Al_2O_3 washcoat to cordierite reduced the operating temperature to 1550°C and gave recoveries of 93.8% Pt and 98.9% Rh.

Of the fluxes used CaO gave the least amount of fume, an operating temperature similar to cordierite, and good coalescence of the collector with recoveries of 94.3% Pt and 98.5% Rh.

*Trade Mark

TABLE 1

Ex	Charge Flux	Wt% Flux Added	Collector	Temp °C	* Holding Time (Min)	Visual Examination	% Recovery		Remarks
							Pt	Rh	
1	5 kg Autocat crushed to minus 8 mesh (2.8mm)	-	5% cast iron shavings	1700	15	Poor separation, large no. prills	-	-	Graphite crucible
2	As Ex. 1 + MgO. SiO ₂ to convert Al ₂ O ₃ washcoat to cordierite	30	5% Fe powder	1540	None	Numerous prills	-	-	-
3	As Ex. 2	30	Ditto	1540	15	Good separation, minimal prills	93.8	98.9	-
4	As Ex. 2	30	2% cast iron shavings	1550	30	Ditto	91.7	98	Effect of reducing iron collector to 2% and increasing holding period
5	As Ex. 2	30	5% cast iron shavings	Variable	30	Several large prills, poor coalescence	-	-	Several operational problems
6	As Ex. 2 + CaO	30% MgOSiO ₂ 10% CaO	Ditto	1470	15	Clean separation almost complete coalescence	83.9	94.5	Poor mass balance (probably due to lock up/contamination in charge mechanism)
7	As Ex. 1 + Fe ₂ O ₃ + Fe powder	10 3.3	Ditto	1560	15	Fair separation, large amount of iron collector present	-	-	Large amount of fume, All Fe ₂ O ₃ added appears to have been reduced by Fe to FeO
8	As Ex. 1 + CaO	10	Ditto	1550	15	Good separation	94.3 96.1	98.5	Slag treated on low intensity magnetic separator
9	As Ex. 1 + CaF ₂	10	Ditto	1550	15	Good separation	91.9	98.1	Lot of fume evolved
10	As Ex. 1 + CaO (10 kg charge)	10	2% cast iron	1550	15	Good separation	86.8	96.3	Crucible leaked near end of trial resulting in some loss of slag.

* Optical pyrometer

The slag from Example 8 (autoemission control catalyst + 10% CaO flux) was ground to 80% minus 100 mesh, mixed with water to form a slurry containing 15% solids and passed through a low intensity (1200 gauss) wet drum magnetic separator. A magnetic concentrate totalling 2% of the input material was obtained. The assays of the products were as follows:

	<u>Pt %</u>	<u>Rh %</u>	<u>Fe</u>
Input slag	0.01	0.0003	
Magnetic concentrate	0.187		6.58
10 Discard slag	0.0085	-	0.37
Recalculated head	0.012		

The platinum recovery from the slag after magnetic scavenging was 31%.

Changes in rhodium concentrate at these low levels was not taken into account. The overall platinum recovery from the catalyst after magnetic scavenging was increased from 94.3% to 96.1%. Because of the low concentration of platinum group metals in the magnetic concentrate, it would probably be returned with the feed to the plasma furnace.

20 EXAMPLES 11 TO 15

A summary of these examples, which were conducted using the same furnace as for Examples 1 to 10 but with a Pt/Pd containing monolith autocat, is set out in Table 2.

As before the monolith autocat was ground or crushed to minus 8 mesh but the autocat and Pt reforming catalyst pellets were mixed with the appropriate fluxes and iron collector, as received. The CaO was added as lime (Ca(OH)_2) and CaF_2 and MgO were commercially available powders.

30 The recovery of platinum in Examples 11 to 14 was very similar to platinum recovery in Examples 1 to 10. The recovery

of palladium on the other hand is slightly lower than the recovery of rhodium (i.e. 96.6% as compared with 98.5%).

Recoveries of 95.3% Pt and 96.6% Pd were obtained when cordierite based autocatalyst monoliths were smelted at approximately 1500°C in a static expanded plasma arc furnace with 10% CaO flux additions and an iron collector. Increasing the weight of iron in the charge from 5% to 10% reduced the residual PGMs in the slag from 0.013% to 0.007%. The dust collected accounted for 1.8% of the charge and represented 0.7% of the platinum and 1.5% of the palladium in the input material.

In order to achieve a comparable smelting temperature with pure alumina substrates the amount of fluxes required constitutes 50% of the charge. Although the level of PGMs in the Al_2O_3 -CaO-MgO-CaF₂ slag were of the same order (0.009%) as the monolith trials, the increase in weight of the fluxes resulted in a PGM recovery of only 60% with 4 wt% iron collector. Increasing the latter to 10% and recirculating the Fe-PGM, in order to achieve a reasonable concentration of PGMs in the bullion, should improve the recovery. The results of the initial smelting trials with platinum reforming catalyst using a CaO-MgO flux addition and 2.5% iron collector showed a recovery of 95% Pt and produced a bullion containing 16.78% Pt.

10

20

1162054

TABLE 2

Ex	Charge	Flux (wt%)	Collector	Feed Rate kg/min	Temp °C	Holding Time (Min)	Visual Examination	% Recovery			Remarks
								Pt	Rh	Pd	
11	5kg Autocat crushed to min- us 8 mesh + CaO	10	5% cast iron turn- ings	1	1500	15	Good coalescence, separation from slag easy	-	-	-	Suprex crucible
12	As Ex. 11	10	10% Fe	.1	1510	15	Ditto	95.3	96.6	96.6	Collector Fe-PGM from Ex. 11 + 5% virgin Fe. Superstar crucible
13	4.9 kg autocat- alyst Alumina pellets (3mm x 6mm) + CaO	100	2.5 cast iron turn- ings	1	1420	15	large prills trap- ed in slag. poor coalescence	-	-	-	Salamander crucible
14	2.5kg autocat- alyst pellets 1.5kg CaO 0.5kg MgO 0.5kg CaF ₂	100	5% Fe	0.7	1475	15	a number of prills in base of slag	60	62	62	Salamander crucible
15	5.0kg Pt refr- aming catalyst 1.7mm dia pellets 3.9kg CaO 1.0mgO	100	2.5% cast iron turn- ings	0.5	1500	15	good coalescence only two large prills	95	-	-	Suprex crucible

X

EXAMPLES 16 TO 20

These Examples relate to trials conducted in an extended arc furnace supplied by University of Toronto, Canada, using Pt/Pd containing refractory substrates, the substrate in each case being ground to minus 60 mesh.

The best recoveries of 74% Pt and 70% Pd were achieved with only 2.6% Fe collector and a slag composition similar to that used in the expanded plasma arc furnace. The residual PGM content of the slag was 0.006. Full results are set out in

10 Table 3.

EXAMPLE 21

This example relates to a trial conducted in a furnace supplied by Technology Application Services Corporation, of North Carolina, U.S.A. The trial was conducted using a pellitised charge including a crushed cordierite monolith, flux and collector. The result is set out at the foot of Table 3.

TABLE 3

Ex	Charge	Flux (wt%)	Collector	Feed Rate kg/min	Temp °C	Holding Time (Min)	Visual Examination	% Recovery	Remarks
16	1kg Autocatalyst + CaO	10	10% Iron Powder	0.25	1600	15	good coalescence but a number of prills		
17	500g Autocatalyst pellets 250g CaO 250 SiO ₂	100	10% iron shot	0.25	1600	5	good coalescence fewer prills than in Ex. 16	53	Considerable loss of collector and gain in weight of slag
18	500g Autocatalyst pellets 300g CaO 100g CaF 100g MgO	100	10% iron shot	0.25	1600	5		74	As Ex. 17
19	1.0kg monolith autocatalyst 100g CaO	10	20% iron shot	0.25	1600	8	good coalescence few prills	65	
20	500g Autocatalyst pellets 400g CaO 100g MgO	100	10% iron shot	0.25	1600	8		53	62.5
21	Pelitised Charge autocat monolith 13.67kg +CaO+ 2% binder	10	10% Fe	1	1550	15		97	97

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the recovery of platinum group metals deposited on or contained in a refractory ceramic substrate containing an aluminium-silicate and/or alumina comprising preparing, in divided form, a charge containing the refractory ceramic substrate bearing the said metals, one or more fluxes, and a collector material or collector material precursor, for the metal or metals to be recovered, heating the charge to a temperature of at least 1420°C to produce a molten metallic phase containing a substantial proportion of the said metal or metals formerly deposited on or contained in the substrate, and a molten slag phase containing flux, ceramic residues and the remainder of the said metals, separating the two phases, and separating the platinum group metals from the metallic phase.
2. A process according to claim 1, wherein the flux or fluxes are selected from the group consisting of CaO, CaF₂, BaO, Fe₂O₃, MgO, SiO₂ and TiO₂.
3. A process according to claim 1 or claim 2 wherein the charge is heated to a temperature in the range 1500-1750°C.
4. A process according to claim 1 wherein the charge is heated in a high intensity heating furnace.
5. A process according to claim 4 wherein the said furnace is a plasma arc furnace.
6. A process according to claim 5 wherein the gas for the plasma arc is selected from the group consisting of Argon, Helium, Nitrogen and Air.

- 15 -

7. A process according to claim 2 wherein the flux content of the charge is up to 100% by wt. of the refractory ceramic substrate content of the charge.

8. A process according to claim 7 wherein the flux content of the charge is 10% by wt of the refractory ceramic substrate content of the charge.

9. A process according to claim 1 wherein the collector material content of the charge is 2 to 10% of the refractory substrate content of the charge.

10. A process according to claim 1 or 9 wherein the collector material is selected from the group iron, nickel, copper, cobalt, lead and aluminium, or mixtures thereof.

11. A process according to claim 1 or 9 wherein the collector material comprises iron powder or filings, iron sponge or cast iron shavings.

12. A process according to Claim 1 in which the collector material precursor is an oxide of iron and a reducing agent.

13. A process according to claim 12 in which the oxide of iron is hematite and the reducing agent is carbon.

14. A process according to claim 1 wherein the refractory ceramic substrate is reduced to finely divided form by crushing or the like.

15. A process according to Claim 14 wherein the finely divided substrate has a mesh size in the range minus 10 to minus 200 mesh.

16. A process according to claim 14 wherein the substrate in finely divided form is mixed with the flux or fluxes and collector material, and the charge so produced is compacted to form charge pellets.

17. A process according to claim 16 wherein 2% by wt of a binder material is added to the finely divided charge.

18. A process according to claim 1 wherein the substrate is in the form of autoemission control catalyst pellets.

19. A process according to claim 1 wherein the substrate is an alumina wash-coated aluminium silicate.

20. A process according to claim 19 wherein the flux comprises MgO and/or SiO₂ whereby during heating at least some of the alumina wash-coat is converted to an aluminium silicate.

21. A process according to claim 19 or claim 20 wherein the aluminium silicate is cordierite.

22. A process according to claim 1 wherein the substrate consists of alumina and the flux content of the charge is approximately equal in weight to the alumina content.

23. A process according to claim 5 and which is a batch process wherein the divided charge is fed into the furnace through the plasma arc and wherein discharge of the plasma arc is

continued for a minimum holding period after passing the entire charge therethrough.

24. A process for the recovery of platinum group metals present in artefacts comprising a refractory ceramic substrate having the platinum group metal deposited on or contained in the refractory ceramic substrate, the said substrate containing an aluminium-silicate, and/or alumina, said process comprising preparing in divided form, a charge containing the refractory ceramic substrate bearing the said metals, one or more fluxes, and a collector material or collector material precursor, for the metal or metals to be recovered, heating the charge to a temperature in the range 1500-1750°C in a high intensity plasma arc furnace to produce a molten metallic phase containing a substantial proportion of the said metal or metals formerly deposited on or contained in the substrate, and a molten slag phase containing flux, ceramic residues and the remainder of the said metals, separating the two phases, and separating the platinum group metals from the metallic phase, the collector material comprising iron powder or filings, iron sponge or cast iron shavings.

**SUBSTITUTE
REPLACEMENT**

SECTION is not Present

Cette Section est Absente